

*Досліджено вплив складу полілігандних цитратно-дифосфатних електролітів та режимів плазово-електролітичного оксидування на процеси формування металооксидних каталізаторів  $TiO_x \cdot MO_y$  ( $M=Fe, Co, Ni$ ). Показані шляхи керування морфологією поверхні, хімічним складом покривів та інкорпоруванням в них оксидів металів тріади заліза. Встановлено, що одержані змішані оксидні покриття характеризуються підвищеною корозійною стійкістю та високою каталітичною активністю в реакціях окиснення монооксиду вуглецю*

*Ключові слова: каталізатор, оксиди титану, оксидні покриття, плазово-електролітичне оксидування, каталітична активність*

*Исследовано влияние состава полилигандных цитратно-дифосфатных электролитов и режимов плазменно-электролитического оксидирования на процессы формирования металлооксидных катализаторов  $TiO_x \cdot MO_y$  ( $M=Fe, Co, Ni$ ). Показаны пути управления морфологией поверхности, химическим составом покрытий и инкорпорированием в них оксидов металлов триады железа. Установлено, что полученные смешанные оксидные слои характеризуются повышенной коррозионной стойкостью и высокой каталитической активностью в реакциях окисления монооксида углерода*

*Ключевые слова: катализатор, оксиды титана, оксидные покрытия, плазменно-электролитическое оксидирование, каталитическая активность*

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# EXAMINING THE FORMATION AND PROPERTIES OF $TiO_2$ OXIDE COATINGS WITH METALS OF IRON TRIAD

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## 1. Introduction

Intensive economic activity and increase in the production capacities of different sectors of industry lead to the growth of the pollution of air and water basins by toxic substances of different nature and chemical stability. Given this, the organization of removal of natural and technogenic contaminants from air and aqueous medium is impossible without the use of effective and accessible catalysts.

At present, however, there is no a universal device or a substance, which makes it possible to solve the indicated problem. Nevertheless, the attention of researchers is drawn among many applied materials to the oxides of titanium [1]. Catalysts based on  $TiO_2$  possess a wide spectrum of functional properties, because of which they are effectively employed in the organic synthesis [2], chemical [3] and paint and varnish industry [4], in the systems of air [5, 6] and water purification [7, 8]. Of particular scientific interest, due to the high chemical inertness, affordability, low toxicity of the products of purification, are the photocatalysts based on  $TiO_2$  [9, 10].

However, the analysis of existing technical solutions, development and improvement of methods for obtaining the effective metal oxide catalysts remain relevant.

## 2. Literature review and problem statement

In the heterogeneous catalysis, the most common are the catalysts based on titanium dioxide in the form of powders with different dispersiveness [11]. The higher catalytic properties in this case are demonstrated by the nano-structured oxide systems that have large specific surface [12].

It should be noted, however, that from the point of view of the application convenience, a better technological form of a catalyst are the thin-film oxide coatings, formed directly on the main metal-carrier by the method of plasma-electrolytic oxidizing (PEO).

A plasma-electrolytic treatment of titanium in the electrolytes of different composition makes it possible to obtain in one stage the uniform coatings of titania. The matrix of base metal is incorporated with the oxides of components of electrolyte, as well as the products of thermochemical and

electrochemical transformations. The composition and properties of the formed oxide layers depend on the nature of oxidized metal, parameters of the electrolysis process and the components (dopants) of the utilized electrolytes [13, 14]. Of special interest is the oxide systems with nonstoichiometric composition, since the rate of electrochemical and chemical processes grows at an increase in the degree of deviation from the stoichiometry.

In order to enhance the functional properties of the obtained oxide systems, the composition of surface layers can additionally be introduced with the nonmetals, the transition, rare and trace elements.

In article [15], PEO of titanium in orthophosphoric acid with the addition of copper nitrate made it possible to obtain porous oxide coatings of titanium phosphates with the inclusions of copper ions. Such coatings possess bactericidal properties.

The authors of [16] received composite coatings  $\text{Ti}/\text{Ti}_n\text{O}_m\text{Zr}_x\text{O}_y$  that demonstrate photocatalytic properties by oxidizing the titanium in electrolytes with the addition of zirconium oxide.

In order to increase the catalytic activity, it is also expedient to introduce ions of the polyvalent metals into the composition of materials [17].

The authors of [18] formed on the alloys of titanium and aluminum the oxide-phosphate coatings doped with nickel and iron at the anodic and anode-cathode polarization of working electrodes. The increased chemical and thermal resistance characterizes the obtained systems.

In paper [19], the mixed oxide systems doped with manganese are synthesized by the oxidizing in the electrolyte based on potassium permanganate.

To obtain the PEO-coatings on valve metals, it is also possible to use polyphosphate electrolytes. In paper [20], authors obtained the oxide coatings of nickel and zinc with a broad range of the concentrations of dopants. Article [21] is devoted to the formation of mixed oxide systems  $\text{Ti}_x\text{Zn}_y\text{O}_z$  from the alkaline electrolytes based on diphosphate with the addition of zinc oxide. In paper [22], silicate electrolyte with the addition of cobalt acetate was used to obtain the oxide coatings of titanium with cobalt. The PEO of titanium was conducted in one stage at effective current density  $10\text{--}20\text{ A/dm}^2$  during 10 min. In order to increase the catalytic activity of coatings in the CO oxidation reaction, the impregnation and annealing of the obtained oxide systems were additionally used.

In order to optimize the technological process of obtaining the catalytically active materials, it is expedient to use plasma-electrolytic oxidizing. This regime of synthesis of the mixed oxide systems makes it possible to incorporate, in one stage, active constituents into the matrix of oxide of a base metal. This will allow receiving functional materials with the high content of dopants and with a wide scope of application.

### 3. The aim and tasks of the study

The aim of present work is a single-stage formation on the titanium alloys by the method of plasma-electrolytic oxidizing of  $\text{TiO}_2$  functional coatings with metals of iron triad.

To achieve the set aim, the following tasks are to be solved:

- to substantiate the selection of components of electrolytes for obtaining the  $\text{TiO}_2$  oxide coatings with metals of iron triad;

- to propose the mode of plasma-electrolytic oxidizing for receiving the catalysts based on titanium oxide with transition metals;

- to establish a relation between the composition of electrolyte and the content of alloying additives in the oxide coatings;

- to examine the composition, morphology and properties of the obtained metal-oxide systems.

## 4. Procedure for obtaining the oxide coatings of titanium dioxide with metals of iron triad, a study of the composition, morphology and properties

### 4. 1. Electrolytes and PEO modes

The coatings with complex oxides  $\text{TiO}_x\text{MO}_y$  ( $M = \text{Fe, Co, Ni}$ ) were formed on the alloys of titanium VT1-0 and OT4-1 by the method of PEO under galvanostatic mode with the use of the direct current source B5–50 at current density  $1\text{--}5\text{ A/dm}^2$ , voltage  $120\text{--}160\text{ V}$ . Electrochemical treatment was conducted in the solutions that contained diphosphate, citrate of alkali metal, as well as the cations of coprecipitated metals  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  (Table 1). The process of oxidizing was carried out for  $30\text{--}60$  minutes at constant agitation of the electrolyte. The flow circulation cooling maintained temperature within the limits of  $20\text{--}25\text{ }^\circ\text{C}$ .

Table 1

Composition of electrolytes and parameters of the synthesis of oxide systems

No.	Electrolyte composition		Current density $i$ , $\text{A/dm}^2$	Voltage sparking $U_s$ , V	Maximum voltage, $U_{\text{max}}$ , V
	Components	Concentration, $\text{mol/dm}^3$			
1	$\text{K}_4\text{P}_2\text{O}_7$ $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ $\text{FeSO}_4$	0.3 0.1 0.1	1.0–5.0	75–80	120–135
2	$\text{K}_4\text{P}_2\text{O}_7$ $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ $\text{CoSO}_4$	0.3 0.1 0.1		80–85	130–140
3	$\text{K}_4\text{P}_2\text{O}_7$ $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ $\text{NiSO}_4$	0.3 0.1 0.1		90–95	145–160

A pretreatment of the samples included mechanical cleaning from the technological impurities, degreasing in the  $0.2\text{--}0.3\text{ M}$  solution of  $\text{NaOH}$ , etching in the mixture of acids  $0.1\text{--}0.3\text{ M}$   $\text{HF}$  and  $0.3\text{--}0.9\text{ M}$   $\text{HNO}_3$ , washing with the distilled water.

### 4. 2. Methods of examining the oxide coatings of titanium dioxide with metals of iron triad

In order to explore the morphology of surface of the obtained catalytic materials, we used the scanning electronic microscope ZEISS EVO 40XVP (Germany). Chemical composition of the surface oxide layers was determined on the energy-dispersion spectrometer Oxford INCA Energy 350 (Great Britain) with the integrated programming environment SmartSEM.

Research of corrosion behavior of titanium alloys with the oxide coatings was conducted by the method of impedance spectroscopy using the automatic alternating-current bridge P-5083 (Ukraine) in the range of frequencies  $20\text{--}1 \times 10^5\text{ Hz}$  in the medium of  $0.1\text{ M}$   $\text{NaCl}$  by sequential scheme

with the use of auxiliary electrodes – the coplanar plates made of corrosion-resistant steel X18H10T [23].

Catalytic activity of the oxide systems was tested in the reaction CO oxidation in CO<sub>2</sub>. Experimental studies were carried out using the laboratory bench in a tubular flowing reactor, as it is indicated in article [24].

## 5. Results of obtaining the oxide coatings on the alloys of titanium

As was previously demonstrated [19, 24], the use of diphosphate electrolytes for the PEO of aluminum and titanium alloys makes it possible to obtain oxide systems with different content of metals in a coating.

In order to form the mixed oxides of TiO<sub>2</sub> with metals of iron triad (Fe, Co, Ni), the composition of working solutions is introduced with an additional ligand – citrate-ion. This ensures an increase in the stability and operation period of the utilized electrolytes due to the formation of sufficiently stable complexes of the composition [MCit]<sup>-</sup> [25], and it also contributes to the more uniform distribution of metals-dopants in coatings.

The chronograms of interelectrode voltage for the mixed oxide coatings (Fig. 1) take a classical form with three characteristic sections. In the pre-spark region (section 1), the U(t)-dependences are practically linear since in the first 2–3 minutes there occurs the formation of the barrier titanium oxide with the current output close to 100 %.

In the electrolytes that contain Fe(II) and Co(II), the oxidation of particles and formation of the mixed oxides of TiO<sub>2</sub>·M<sub>3</sub>O<sub>4</sub> occurs even in the pre-spark region (Fig. 1).

With the onset of sparking (section 2), an increase in the voltage considerably slows down as a result of the breakdown of TiO<sub>2</sub> barrier film, the rate of formation of titania is lowered, and the oxides of M<sub>3</sub>O<sub>4</sub> dopants undergo thermal decomposition. A transition into the region of micro-arcs (section 3) is characterized by insignificant change in the voltage and by relative stability of the process while the range of PEO voltages is in the interval of 120–160 V.

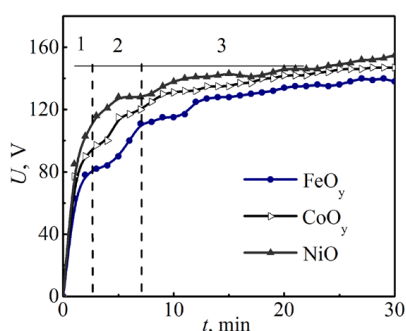


Fig. 1. Chronograms of interelectrode voltage of the systems based on titanium oxides and metals of iron triad: 1 – pre-spark region, 2 – region of sparking, 3 – region of micro-arcs. Ion-dopant concentration in the electrolyte is 0.1 mol/dm<sup>3</sup>. Current density is 1 A/dm<sup>2</sup>

It was established that the dependence of spark voltage on the concentration of dopant is linear for all electrolytes (Fig. 2). The spark voltage grows in a series Fe<Co<Ni.

Dependences of the rate of change in voltage dU/dt on the applied voltage (Fig. 3) are also analogous for all dopants by form.

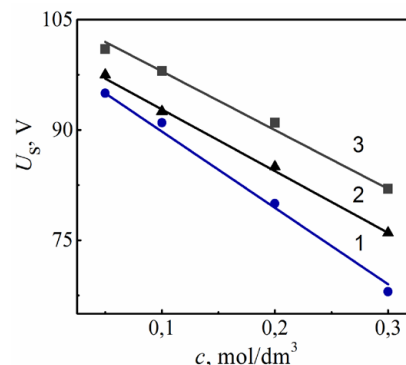


Fig. 2. Dependences of spark voltage on the concentration of dopant in the diphosphate-citrate electrolyte: 1 – Fe<sup>2+</sup>; 2 – Co<sup>2+</sup>; 3 – Ni<sup>2+</sup>

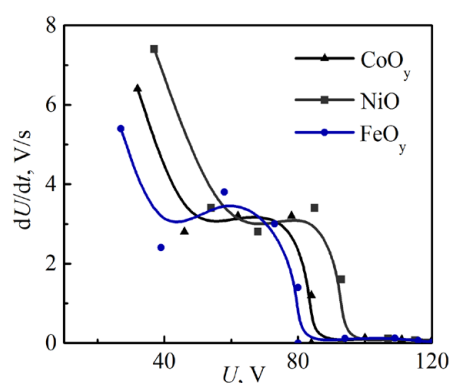


Fig. 3. The rate of change in the interelectrode voltage of the mixed oxide coatings vs the voltage. The concentration of dopant is 0.1 mol/dm<sup>3</sup>. Current density is 1 A/dm<sup>2</sup>

The extremum, related to the thermal dissociation of the oxides of polyvalent metals, occurs in the transition to the region of sparking on all dependences.

Results of microscopic examinations of the morphology of coatings TiO<sub>x</sub>·FeO<sub>y</sub>; TiO<sub>x</sub>·CoO<sub>y</sub> and TiO<sub>x</sub>·NiO testify to the formation a toroidal structure of surface (Fig. 4); in this case, the porosity of coatings is lower in comparison with the oxide systems TiO<sub>x</sub>·MnO<sub>y</sub> [24].

In the course of studies of the element composition of the coatings, synthesized on the alloy OT4-1, we discovered (Table 2) the traces of manganese.

Table 2

Element composition of coating with the mixed oxides on the alloy OT4-1

Electrolyte	Element composition, % by mass									
	C	O	Na	P	K	Ti	Mn	Fe	Co	Ni
1	5.98	46.06	1.24	17.07	5.56	18.38	0.19	5.23	–	–
2	6.22	44.54	1.39	16.60	7.24	15.82	0.23	–	7.76	–
3	6.24	46.28	0.58	16.59	4.94	21.65	0.22	–	–	3.17

On the alloy OT4-1, we also obtained a mixed oxide system, which includes all metals form the family of iron (Fig. 5). The formed coating has the following composition, % by mass: Ti – 16.54; O – 44.73; P – 16.7; Fe – 2.05; Co – 2.74; Ni – 2.36, the rest are impurities.

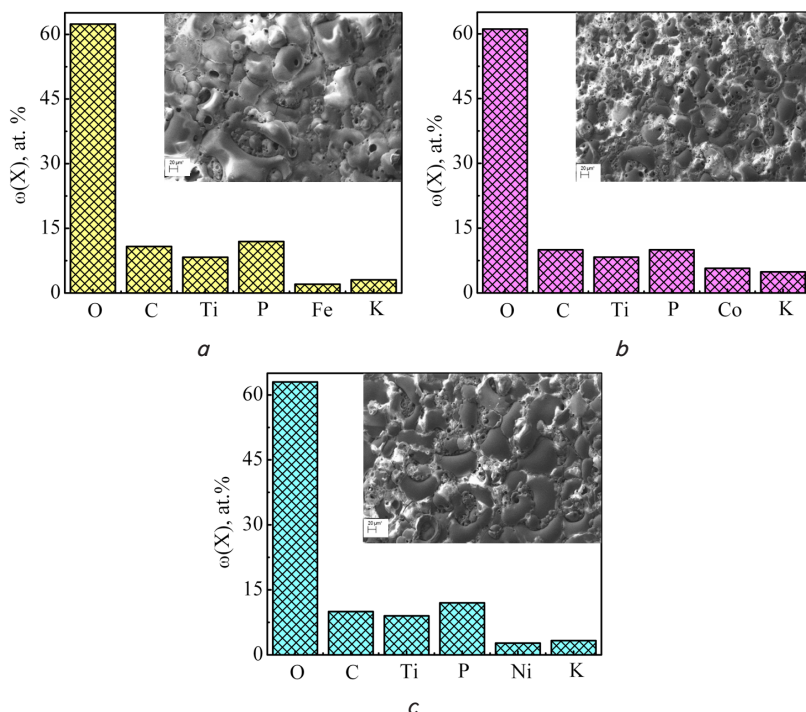


Fig. 4. Microphotographs of the surface, and the composition of oxide coatings on BT1-0: *a* –  $\text{TiO}_x\text{-FeO}_y$ ; *b* –  $\text{TiO}_x\text{-CoO}_y$ ; *c* –  $\text{TiO}_x\text{-NiO}$ . Magnification  $\times 200$

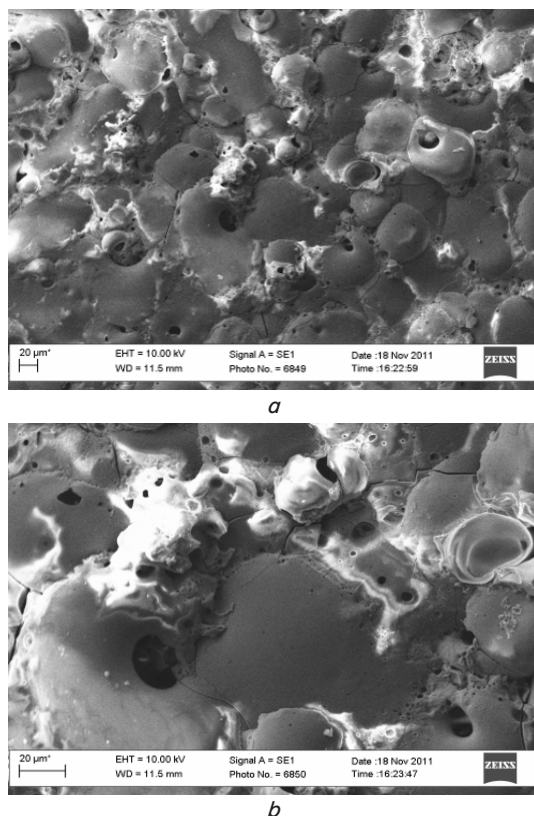


Fig. 5. Microphotographs of the surface of coating with the mixed oxides  $\text{TiO}_x\text{-(FeCoNi)O}_y$  on OT4-1: *a* – magnification  $\times 200$ ; *b* – magnification  $\times 500$

According to the results of testing the corrosion resistance of the mixed  $\text{TiO}_2$  coatings with metals of iron triad, we determined the deep corrosion indices  $k_h$  (Fig. 6).

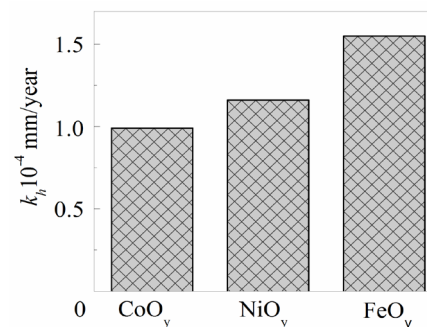


Fig. 6. Deep corrosion index of metal oxide systems  $\text{TiO}_x\text{-MO}_y$  in 0.1 M NaCl

Testing the catalytic activity of coating with the mixed titanium oxides with nickel, cobalt and iron is carried out in the model reaction of oxidation of carbon oxide (II). It was established that the ignition temperature  $T_i$ , which matches the start of effective work of the catalyst, is in the interval of 250–270 °C, whereas for platinum it is 200 °C. The oxide systems  $\text{TiO}_x\text{-CoO}_y$ ,  $\text{TiO}_x\text{-NiO}$ ,  $\text{TiO}_x\text{-FeO}_y$  at 420 °C ensure the degree of CO conversion at 68 %, 57 % and 46 %, respectively (Table 3). Complete conversion of carbon mono-oxide on these materials is achieved at temperature higher than 500 °C.

Table 3

Characteristics of coating with the mixed oxides

Electrode material	Content of alloying component $\omega$ , % by weight	Conversion degree X, %	Ignition temperature $T_i$ , °C
Pt [25]	100	100	200
Pt <sub>exp</sub>	100		
$\text{TiO}_x\text{-CoO}_y$	Co–7.7	68	280
$\text{TiO}_x\text{-NiO}$	Ni–3.2	57	270
$\text{TiO}_x\text{-FeO}_y$	Fe–5.2	46	290

## 6. Discussion of the composition, morphology and properties of the oxide coatings on titanium alloys

The character of chronograms of the interelectrode voltage (Fig. 1), the antibatic dependence of spark voltage on the concentration of dopant in the electrolyte (Fig. 2), as well as impact of the nature of cation-dopant on the spark voltage (Fig. 3), all are predetermined by a number of circumstances.

First, iron and cobalt, in contrast to nickel, are the polyvalent metals; therefore, they can form a number of oxides with variable composition, including those nonstoichiometric ( $\text{M}_3\text{O}_4$ ) that are the systems of the spinel type. It should be noted that the stability of oxidation degree +3 decreases in a series  $\text{Fe} > \text{Co}$ .

Second, the oxides of different composition differ by the value of specific resistivity (Table 4), which depends on the number of cation vacancies and oxygen in a crystal lattice, as well as on temperature. The thermal resistance of oxides is reduced both with the increase in the metal oxidation



number and in a series:  $\text{Fe}_3\text{O}_4 > \text{Co}_3\text{O}_4$ ; the oxides of the MO composition prove to be the most thermoresistant.

Table 4

Specific resistivity and thermal resistance of the oxides of iron triad metals

Metal	Oxide	Specific resistivity $\rho$ ( $\Omega\cdot\text{cm}$ ) at 293 K	Thermal resistance
Fe	FeO	$10^5\text{--}10^8$ semiconductor of the p-type	—
	$\text{Fe}_2\text{O}_3$	$10^5\text{--}10^8$	1500–1690 K $6\text{Fe}_2\text{O}_3 \rightarrow 4\text{Fe}_3\text{O}_4 + \text{O}_2$
	$\text{Fe}_3\text{O}_4$	$4\cdot 10^{-3}$ degenerated semiconductor	$T > 1900$ K $2\text{Fe}_3\text{O}_4 \rightarrow 6\text{FeO} + \text{O}_2$
Co	CoO	$10^6\text{--}10^{10}$	—
	$\text{Co}_3\text{O}_4$	$4\cdot 10^3\text{--}10^5$	1200–1230 K $2\text{Co}_3\text{O}_4 \rightarrow 6\text{CoO} + \text{O}_2$
Ni	$\text{Ni}_{1-x}\text{O}$	$10^6\text{--}10^{13}$	—
	NiO	$10^{13}\text{--}10^{15}$	—

A decrease in  $dU/dt$  in the pre-spark region (Fig. 2) is caused by the oxidation of the cations of dopants and by incorporation in the composition of the surface layer of more electro-conductive oxides and hydroxides. For the nickel-containing electrolytes, the appearance of an extremum is caused by the formation of cation vacancies and by the corresponding increase in the specific electrical conductivity. Further reduction in the rate of change in voltage in the region of sparking and micro-arc discharges is connected with an increase in the thickness of coatings and the introduction of the oxides of dopants during a stable degree of oxidation.

An analysis of surface morphology of the synthesized oxide systems (Fig. 4) allows us to draw a conclusion that the highest content of dopant and the minimum size of grain, other conditions being equal (identical concentration of salts in the electrolyte and unchanged modes of electrolysis), are demonstrated by the systems  $\text{TiO}_x\text{-CoO}_y$ .

At the surface of systems  $\text{TiO}_x\text{-CoO}_y$  (Fig. 4, a) there appear spheroids, as a result it becomes more developed and relief. The nickel-containing mixed oxides are characterized by the formation of larger globules, which overlap pores (Fig. 4, c).

An analysis of the element composition of oxide systems (Fig. 4) indicates the inclusion in the matrix of Titania of alloying metals Fe, Co, Ni, as well as phosphorus and potassium. The content of dopants in coatings grows with an increase in the current density and ratio of the concentrations of ligands diphosphate/citrate.

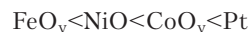
Manganese is included into the composition of alloy OT4-1 in the amount of 0.7–2.0 % by mass. That is why the presence of this element in the coatings (Table 3) is predetermined by the formation of its oxides in the process of PEO. There is a possibility of an alternative two-stage path for the inclusion of manganese into the composition of coatings. The ionization of manganese and the transition into the electrolyte with the formation of complex particles occur at the initial stage. At the second stage, under the action of electrical discharges, there is the incorporation of manganese oxides into the composition of the formed layers.

Compositional analysis of the mixed oxide system  $\text{TiO}_x \times (\text{FeCoNi})\text{O}_y$  reveals that the content of dopants in a coat-

ing differs unessentially since the salt concentration in the electrolyte is identical. A smaller amount of iron is explained by the formation in the solution of more stable complexes Fe(II) with both ligands [26, 27]. The stability of electrolyte in this case substantially grows. The complexes of cobalt with citrate- and pyrophosphate ions are the least stable, which explains its content in the coating, the largest in the row of the indicated metals. The morphology of surface of a multicomponent oxide includes elements of all three types of the structures: microporous, characteristic for  $\text{TiO}_x\text{-CoO}_y$ , globular relief of  $\text{TiO}_x\text{-NiO}$  and toroidal of  $\text{TiO}_x\text{-FeO}_y$ .

Results of testing the corrosion resistance of oxide systems testify to the high protective properties of the coatings, which contain oxides Fe, Co and Ni. The  $\text{TiO}_x\text{-CoO}_y$  coatings manifest the largest corrosion resistance among the systems being investigated.

An analysis of the catalytic activity of coating with the mixed oxides in the reaction of CO oxidation testifies to an increase in the conversion degree in the row:



and reduction in the ignition temperature in the row:



Based on the aforementioned, it is possible to argue that Pt, the oxides of  $\text{FeO}_y$  and NiO demonstrate high catalytic activity in the reaction of oxygen release with the formation of the O–O bond. The  $\text{CoO}_y$  system is distinguished by high activity in the oxidation processes, which are accompanied by the destruction of the O–O bond. This particular influence ensures an increase in the rate of CO oxidation to  $\text{CO}_2$ .

Thus, the mixed oxide systems  $\text{TiO}_x\text{-MO}_y$  ( $M=\text{Mn, Fe, Co, Ni}$ ) of the varied thickness and morphology, obtained as a result of PEO of titanium alloys, can find their application in the catalytic systems of air and water purification.

## 7. Conclusions

1. We substantiated the choice of component composition of PEO electrolytes of titanium alloys for the formation of coating with the mixed oxides with metals of iron triad. The citrate-pyrophosphate electrolytes are proposed with the addition of sulfates of iron triad metals for the formation of oxide systems with a varied content of dopants. The introduction of an additional ligand contributes to an increase in the stability, operation period of working solutions and to the more uniform distribution of metals-dopants in the coatings.

2. A technique for obtaining the metal-oxide catalysts  $\text{TiO}_x\text{-MO}_y$  ( $M=\text{Fe, Co, Ni}$ ) by the method of plasma-electrolytic oxidizing is proposed. The electrochemical treatment of titanium alloys in the citrate-diphosphate electrolytes at voltage 120–160 V makes it possible to form the mixed metal-oxide systems with the content of iron triad metals at 3–8 at. %. It is shown that the antibatic dependence of spark voltage on the concentration of dopant in an electrolyte is caused by an increase in electrical conductivity of the growing mixed oxide as a result of the higher conductivity of oxides of dopants.

3. Depending on the nature of dopant, the surface of coating with mixed oxides has a different structure. The Ti-

$\text{O}_x\text{-CoO}_y$  coatings are microporous, the  $\text{TiO}_x\text{-NiO}$  coatings have a globular relief, the  $\text{TiO}_x\text{-FeO}_y$  coatings are toroidal. The porosity and size of the grains of coating with the mixed oxides grow in the row of dopants cobalt – nickel – iron.

4. The obtained oxide coatings are characterized by the developed toroidal surface, enhanced corrosion resistance and high catalytic activity in the carbon (II) oxide conversion reaction.

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